Galvanosorptive reaction process

The invention relates to a galvanosorptive reaction process for converting sorptive reaction work into useful electrical work by means of a galvanic reaction cell comprising feeding to and carrying off a ternary substance system consisting of a carrier gas vapor mixture and a solution absorbing the vapor component in the cell housing, as well as the formation of the fed-in and carried-off substance flows into an isobaric substance circuit with thermal decomposition of the solution and separation of the solution components outside the reaction cell.

A galvanic reaction cell of a modified type, with hydrogen and an aqueous ammonia solution in an isobaric substance circuit with thermal decomposition of the solution and re-liquefaction of the evaporated solution component carried out outside the reaction cell is known from DE 3302635 A1. However, the design of the galvanic reaction cell and the design of the isobaric substance circuit as described in DE 3302535 A1 are disadvantageous for the galvanic reaction mechanism inside the cell and its operational behaviour.

The ammonia being fed in liquefied form on the cathode side to the reaction cell contains residual portions of water, which during the operation is leading to a constant dilution of the liquid ammonia in the reaction cell and thus after a short time

to an operational standstill, because a continuous extraction of diluted ammonia from the cell is lacking. In addition the non-meterable substance circuit gives rise to an unsteady power and voltage behaviour of the reaction cell. Moreover the method, in which the waste heat of the ammonia liquefaction is to be left in the substance circuit and the thermal efficiency of the galvanic energy conversion thereby raised, is based on process features that do not permit a recovery of the liquefaction waste heat, for example the liquefaction of overheated ammonia vapor at a higher temperature than the saturation temperature.

In addition, on account of the low solubility of gaseous hydrogen in liquid ammonia the stoichiometric introduction of the reactants to the reaction zone of the cathode is possible only to a limited extent, which has a diminishing effect on the substance conversion and thus on the electrical energy yield. An additional reduction of the energy yield arises due to the partial vapor pressure drop resulting from the isobaric mixing of hydrogen and liquid ammonia inside the reaction cell.

A different kind of reaction cell with a closed isobaric substance circulation is known from the documents DE-OS 1596143 and DE-OS 1599153. An aqueous hydrogen halide solution acts as the substance system, said hydrogen halide solution being partially decomposed electrolytically, i.e. by adding electrical energy it decomposes to elementary hydrogen and the

corresponding liquid halogen, whereby the decomposition products are fed again to a recombination cell and converted into the aqueous initial solution with the release of electrical energy. Here, a finite amount of ambient heat is to be converted into useful electrical energy, which former ultimately results from the useful voltage difference of both process steps. Use is made inside the recombination cell of the chemical reaction work and not the sorptive reaction work, which is lost with the disclosed recombination cell and therefore can be expended as additional electrical energy in the electrolytic separation.

The basis adopted here was the ideal voltage values of the decomposition and the recombination of the substance system, which are known to represent equilibrium values and consequently do not show any substance conversion into one of the reaction directions. As soon as a noticeable substance conversion is generated, the voltage values of both reaction steps become alike, as a result of which the disclosed work gain is reduced. In addition, the loss of the sorptive reaction work reduces the work gain, so that a technical exploitation of this effect holds out little promise.

Furthermore, there is described in EP 0531293 an isobaric process for the conversion of sorptive reaction work into electrical work with a closed ternary substance circulation with the use of a carrier gas and a thermally decomposable,

sorptively acting aqueous solution, whereby the energy conversion is intended to be carried out in a galvanosorptive reaction cell, the thermal decomposition of the solution and separation of the solution components on the other hand outside the reaction cell. Further galvanosorptive and electrochemical energy conversion processes with isobaric substance circuits are known from EP-OS 91917497. Neither the design of this novel, galvanosorptive reaction cell, nor the reaction mechanisms taking place inside the reaction cell and influencing the design emerge from these two documents, so that an essential prerequisite for the technical exploitation of the principle is lacking.

Therefore, one goal of the invention is the design of a technically exploitable, galvanosorptive reaction cell for the conversion of sorptive reaction work into useful electrical work by taking account of the reaction mechanisms taking place inside the cell in the sorption process. Another goal of the invention is the formation of the fed-in and carried-off substance flows into an operationally stable, regulatable, isobaric substance circuit with high process efficiency, whilst avoiding the previously mentioned disadvantages of the galvanic reaction cell. Furthermore, the invention aims to increase the electrical energy yield of this galvanosorptive reaction cell over and

above the substance conversion by utilising the latent and sensitive heats contained in the substance flows fed into it.

The goal to develop a technically exploitable design of a galvanosorptive reaction cell is reached by combining the features of claim 1 for a membrane electrolyte cell or by combining the features of claim 2 for a liquid gap cell, whereby both cell configurations, without geometric modifications, enable the anion generating and the cation-generating reaction mechanism. With the sorptive liquefaction of the vapor in the solution generating useful electrical work, premature substance conversion limitations of the galvanic reaction cell are removed in an advantageous way for the galvanosorptive cell, for example, the low hydrogen solubility in liquids and the inability of the galvanic cell gain a portion of the liquefaction heat directly as reaction work. Therefore, galvanosorptive reaction cells achieve higher energy yields and efficiencies than galvanic reaction cells.

As described in claim 5 and claim 11 any sorptive liquid mixtures thermally decomposable into a vapor component and an absorbing liquid component can be used in combination with a carrier gas forming ions with the vapor component, i.e. hydrogen or oxygen, in order to start the galvanosorptive reaction process in the galvanosorptive reaction cell.

As described in claim 12 an electrolyte soluble in the solvent with an, in comparison to the partial pressure of the vapor component insignificant inherent vapor pressure can be added to the individual substance system in order to improve the ion conductivity and likewise the internal resistance of the reaction cell can be reduced in an advantageous manner. The structural materials of these reaction cells do however need to be suited to the selected substance system.

Such sorptive liquid mixtures combinable with a carrier gas are for example the aqueous solutions of NH_3, H_2SO_4 or LiBr or the solution $NH_3/LiNO_3$. These and further solutions were investigated by Niebergall in "Working substance pairs for absorption refrigeration systems" in regard to their utility at low temperatures. The low-temperature use of these solutions is also advantageous for the thermo-galvanic energy conversion, because the waste heat of many technical processes can be used as a cost-free, convertible heating energy potential.

According to the process features described in claim 3 or claim 9 the vapor partial pressure difference acting in the galvanosorptive cell between the carrier gas-vapor mixture and the sorptive solution can be raised not only by adjusting the over all system pressure P_{total} and hence by the carrier gas filling, but also by conveying the circulation rate of the vapor-storing carrier gas in the circuit. This gives rise to an

increase in the useful voltage without additional mechanical loading of the built-in cell components, with only slightly higher power consumption of the gas compressor arranged in the external part of the substance circuit. This advantageous possibility is likewise not available with the galvanic reaction cell disclosed in DE 3302635 A1.

The adiabatic running of the process inside the galvanosorptive reaction cell leads to a simplified cell design, because it is possible to dispense heat transfer channels inside the cell. According to the features described in claim 4 or claim 10 such channels are required for the non-adiabatic running of the process. A heat transfer medium for cooling or heating the reaction cell is flowing through these channels. Preferably a solution of the same kind as in the reaction process can be used, which is only in thermal contact with the absorbing solution and the electrode wetted by the solution.

The goal of increasing the electrical energy yield of the galvanosorptive reaction cell is accomplished as described in claim 6 or claim 13 with the assignment of an activation source, which permanently confers a electrostatic voltage difference to the electrodes from the outside with a very low electric current flow, whereby the latter can amount to several volts and is superimposed on the inherent voltage difference of the cell. It gives rise within the reaction cell to a sorptive vapor

liquefaction along with a temperature drop of the concentrating solution, whereby the applied voltage difference is proportional to the temperature drop and inversely proportional to the increase in vapor component concentration of the solution and is available as a working voltage difference at the external load resistor less the cell voltage losses. Using this measure, the power density of the galvanosorptive cell is increasing apart from the useful electrical work yield and the thermal efficiency is rising.

With the combinations of features of claim 7 or claim 14 the substance flows fed to and carried off from the reaction cell are formed into an isobaric, substance circuit, which makes the substance potential difference of the galvanosorptive reaction cell available in an operationally stable fashion, and therefore can be regulated via the flow rates of the conveying devices independent of one another (solution pump and gas compressor) and exhibits a high thermo-galvanic efficiency with the combined process components.

If the electrostatic voltage of the activation source acts on the reaction process inside the galvanosorptive reaction cell, then with the combinations of features of claim 8 or claim 15 the process engineering expenditure in the external part of the substance circuit is clearly simplified and the energy yield of the galvanosorptive reaction cell increased.

The invention is described with the aid of the figures 1 to 7. In detail, the figures show:

Fig. 1: The functional principle and the schematic structure of a universally utilisable, galvanosorptive membrane electrolyte cell, with the exemplified representation of a cation-generating, ternary substance system SI: $[H_2^g, NH_3^v]$ $[NH_4^{+EL}, El]$ $[NH_3^{aq}, H_2^g]$ and an anion-generating, ternary substance system SII: $[O_2^g, H_2O^v]$ $[OH^{-EL}, El]$ $[LiBr^{aq}, O_2^g]$,

Fig. 2: The functional principle and the schematic structure of a universally utilisable galvanosorptive liquid gap cell with the exemplified representation of a cation-generating, ternary substance system SIII: $[H_2^g, H_2O^v]$ $[H_3O^{+aq}, H_2SO_4^{aq}]$ $[H_2SO_4^{aq}, H_2^g]$ and an anion- generating, ternary substance system SIV: $[O_2^g, H_2O^v]$ $[OH^{-aq}, H_2SO_4^{aq}]$ $[O_2^g, H_2SO_4^{aq}]$,

Fig. 3: The cyclic process and the substance states of an adiabatic galvanosorptive reaction cell in a schematic T/ξ and P/ξ diagram for an arbitrary, ion-generating, ternary substance system,

Fig. 4: The functional circuit diagram of a galvanosorptive reaction cell with closed, isobaric substance circuit according to the cyclic process as per Fig. 3,

Fig. 5: The cyclic process and the substance states of the galvanosorptive reaction cell with electrostatic support for an arbitrary, ion-generating, ternary substance system in a schematic T/ξ and P/ξ diagram,

Fig. 6: The functional circuit diagram of a galvanosorptive reaction cell with electrostatic support and closed, isobaric substance circuit in accordance with the cyclic process as per Fig. 5, and

Fig. 7: Schematically, the electrical equivalent circuit diagram of the galvanosorptive reaction cell with assigned activation source.

The structure and mode of functioning of the galvanosorptive membrane electrolyte cell will be explained in greater detail with the aid of the examples of embodiment of Fig. 1.

The membrane electrolyte cell consists of a cell housing (2), which is divided by a media sealing, electrically isolating peripheral seal (3) into a first housing part (2.1) and a second housing part (2.2). The housing (2) contains a flat-shaped, porous, gas-permeable first electrode (4) and a flat-shaped, porous, gas- and liquid-permeable, second electrode (5). Between the electrode's faces (4.2, 5.2) either a selectively cation- or a selectively anion-permeable membrane electrolyte (6) is arranged, which forms a mechanically stable composite unit with

the porous electrodes (4,5). The first electrode face (4.1) facing away from the membrane electrolyte (6) forms a slit-shaped gas channel (7) with the first housing part (2.1), through which a vapor-saturated, cation-generating carrier gas type [G,V] or a vapor-saturated, anion-generating carrier gas type [G,V] is flowing. The second electrode face (5.1) facing away from the membrane electrolyte (6) forms a slit-shaped liquid channel (8) with the second housing part (2.2), through which an undersaturated, vapor-absorbing solution [S] is flowing. The electrodes (4,5) are connected with current lead-in and lead-off devices (9,10) and an external load resistor (11). The current lead-in and lead-off devices (9,10) represented schematically are arranged in Fig. 1 rotated through 90°. They are constructed geometrically like the conduction systems known from fuel cells, so that they only slightly reduce the reactive surfaces of the electrodes and do not hinder the through-flow of the slit-shaped channels (7,8).

As described in Fig. 3 and Fig.4 a vapor-enriched carrier gas [G,V]$_4$, (ZP4) with high vapor partial pressure (P$_T$,P$_{V4}$) is fed via an inlet opening (12.1) in the first housing part (2.1) to the gas channel (7) and a stoichiometric reduced quantity of vapor-depleted carrier gas [G,V]$_1$, (ZP1) with reduced vapor partial pressure (P$_T$,P$_{V1}$) is carried off via an outlet opening (12.2). Via an inlet opening (13.1) in the second housing part

(2.2), an undersaturated depleted solution $[S]_2$, (ZP2) with low vapor component concentration (ξ_{s2}) and low vapor partial pressure (P_T, P_{v2}) is fed to the liquid channel (8) and a two-phase mixture $[S,G,V]_3$ (ZP3) of undersaturated enriched solution $[S]_3$ with high vapor component concentration (ξ_{s3}) and medium vapor partial pressure (P_T, P_{v3}) and a recovered, moderately vapor-enriched carrier gas $[G,V]_3$ in the solution with the same medium vapor partial pressure (P_T, P_{v3}) is carried off via an outlet opening (13.2).
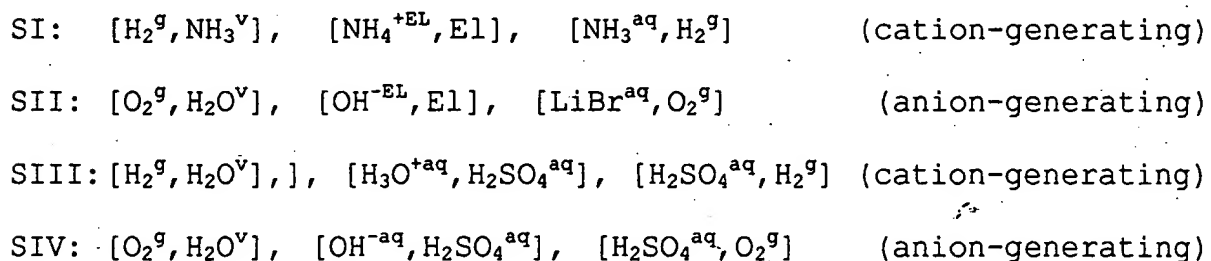
When a cation-generating gas type is being used, as for example hydrogen, and a membrane electrolyte (6) selectively letting through this cation type, cations are formed at the phase boundary (4.2) (gas/solid/electrolyte) of the first electrode (4) as a result of anodic oxidation with the stoichiometric consumption of hydrogen and vapor from the gas channel (7). These cations migrate through the membrane electrolyte (6) to the second electrode (5) and at its phase boundary (5.1) (gas/liquid/solid) increases the concentration of the absorbing solution flowing in the liquid channel (8) as a result of cathodic reduction, with the recovery of an equivalent stoichiometric quantity of hydrogen in the solution. The electrons flow here from the first electrode (4) via the conduction devices (9,10) and the external load resistor (11) to the second electrode (5).

When an anion generating gas type is being used, as for example oxygen, and a membrane electrolyte (6) selectively letting through this anion type, anions are formed at the phase boundary (4.2) (gas/solid/electrolyte) of the first electrode (4) as a result of cathodic reduction with the stoichiometric consumption of oxygen and vapor from the gas channel (7). These anions migrate through the membrane electrolyte (6) to the second electrode (5) and at its phase boundary (5.1) (gas/liquid/solid) increases the concentration of the solution flowing in the liquid channel (8) as a result of anodic oxidation with the recovery of an equivalent stoichiometric quantity of oxygen in the solution. The electrons flow here from the second electrode (5) via the current conduction devices (10,9) and the external load resistor (11) to the first electrode (4).

Circled state points (ZP1 to ZP4), which represent saturation equilibriums for the respective fluid flows, and their definition by state magnitudes $[P,T,\xi s,\xi v]$ are assigned to the fluid flows fed to and carried off from the membrane electrolyte cell according to Fig. 1. They relate to the cyclic process according to Fig. 3. The substance potential difference of the galvanosorptive reaction process inside the membrane electrolyte cell arises with the local assignment of the substance flows on the reaction cell. Therefore, the vapor-saturated gas flow is conveyed with transverse consumption of a stoichiometric

quantity of carrier gas and vapor. This is done preferably in the opposite direction of solution flow, but parallel to the electrode faces through the cell.

An aqueous solution of lithium bromide in combination with oxygen as an anion-generating reaction system (SII) and an aqueous ammonia solution in combination with hydrogen as a cation-generating reaction system (SI) were selected as examples of ternary substance systems for the membrane electrolyte cell. Two other ternary substance systems of aqueous sulphuric acid in combination with oxygen (SIV) and in combination with hydrogen (SIII) are presented in Fig. 2 for the liquid gap cell. In the substance systems (SII, SIII and SIV), water is the vaporising mixture component and in substance system (SI) ammonia. The selected examples of ternary substance systems can be applied to both types of cell structure. The galvanosorptive reaction systems read as follows:

SI: $[H_2^g, NH_3^v]$, $[NH_4^{+EL}, El]$, $[NH_3^{aq}, H_2^g]$ (cation-generating)

SII: $[O_2^g, H_2O^v]$, $[OH^{-EL}, El]$, $[LiBr^{aq}, O_2^g]$ (anion-generating)

SIII: $[H_2^g, H_2O^v]$,], $[H_3O^{+aq}, H_2SO_4^{aq}]$, $[H_2SO_4^{aq}, H_2^g]$ (cation-generating)

SIV: $[O_2^g, H_2O^v]$, $[OH^{-aq}, H_2SO_4^{aq}]$, $[H_2SO_4^{aq}, O_2^g]$ (anion-generating)

The electrode pairs and the membrane electrolytes [EL] are indeed geometrically alike in the selected reaction systems, but differ in their mode of functioning and in the material

structure. The electrode reactions are stated in greater detail for the substance system (SI):

Reaction system (SI): $\alpha | (NH_3^v, H_2^g)^\alpha | NH_4^{+EL}, EL | NH_3^{aq}, H_2^g)^\beta | \beta$

Cathode reaction α: $e^\alpha + NH_4^{+EL} = (NH_3^v + \frac{1}{2}H_2^g)^\alpha$

Anode reaction β: $(NH_3^{aq} + \frac{1}{2}H_2^g)^\beta = NH_4^{+EL} + e^\beta$

Cell reaction $(\alpha+\beta)$: $e^\alpha + (NH_3^{aq} + \frac{1}{2}H_2^g)^\beta = (NH_3^v + \frac{1}{2}H_2^g)^\alpha + e^\beta$

Substance potential

difference: $(\varphi^\beta - \varphi^\alpha)_{st.} = (R \times T / F) \times \ln[(P_\alpha / P_\beta)_{NH3} \times (P_\alpha / P_\beta)^{\frac{1}{2}}_{H2}]$

Electrostatic potential

difference: $(\varphi^\beta - \varphi^\alpha)_{est.} = [Cp \times (T_1 - T_2)_{NH3aq.} \pm Q_{rev.}] / F$

As a further development of the invention, the structure and mode of functioning of a galvanosorptive liquid gap cell are described in greater detail with the aid of the examples of embodiment of Fig. 2.

The liquid gap cell consists of a cell housing (21), which is divided by a media sealing, electrically isolating peripheral seal (22) into a first housing part (21.1) and a second housing part (21.2). The housing (21) contains a flat-shaped, mechanically stable, porous, gas-permeable first electrode (23) and a flat-shaped second electrode (24) lying adjacent, without a gap, to the second housing part (21.2). The face of the first housing part (21.1) and the face (23.2) of the first electrode

(23) facing one another form a slit-shaped gas channel (25), through which a vapor-saturated, cation-generating carrier gas type [G,V] or a vapor-saturated, anion-generating carrier gas type [G,V] is flowing. The electrode faces (23.1) and (24.1) facing one another form a slit-shaped liquid channel (26), through which an undersaturated, vapor-absorbing, ion-conducting solution [S] is flowing. The electrodes (23,24) are electrically connected with the current lead-in and lead-off systems (27,28) and an external load resistor (29). The gas-side current conduction system (27) is constructed geometrically like that of the gas electrodes of fuel cells and is represented schematically in Fig. 2 rotated through 90°.

As described in Fig. 3 and Fig.4 a vapor-enriched carrier gas $[G,V]_4$, (ZP4) with high vapor partial pressure (P_T, Pv_4) is fed to the gas channel (25) via an inlet opening (30.1) in the first housing part (21.1), and a stoichiometrically reduced quantity of vapor-depleted carrier gas $[G,V]_1$, (ZP1) with a reduced vapor partial pressure (P_T, Pv_1) is carried off via an outlet opening (30.2). An undersaturated, depleted solution $[S]_2$, (ZP2) with low vapor component concentration (ξ_{s2}) and low vapor partial pressure (P_T, Pv_2) is fed to the liquid channel (26) via an inlet opening (31.1) in the second housing part (21.2), and a two-phase mixture $(S,G,V)_3$, (ZP3) of undersaturated, enriched solution $[S]_3$, with high vapor component concentration (ξ_{s3}) and

medium vapor partial pressure (P_T, P_{v3}) and a recovered vapor-enriched carrier gas $[G, V]_3$ in the solution with the same medium vapor partial pressure (P_T, P_{v3}) is carried off via an outlet opening (31.2).

When a cation-generating gas type, i.e. hydrogen, is used, cations are formed at the phase boundary (23.1) (gas/liquid/solid) of the first electrode (23) as a result of anodic oxidation with the stoichiometric consumption of hydrogen and vapor from the gas channel (25). These cations migrate transversely through the solution flowing in the ion-conducting liquid gap (32) to the second electrode (24) and at its phase boundary (24.1) (gas/liquid/solid) increases the concentration of the solution flowing in the liquid channel (26) as a result of cathodic reduction with the recovery of an equivalent stoichiometric quantity of hydrogen in the solution. Here, the electrons flow from the first electrode (23) via the current conduction system (27,28) and the external load resistor (29) to the second electrode (24).

When an anion-generating gas type is used, i.e. oxygen, anions are formed at the phase boundary (23.1) (gas/liquid/solid) of the first electrode (23) as a result of cathodic reduction with the stoichiometric consumption of oxygen and vapor from the gas channel (25). These anions migrate transversely through the solution flowing in the ion-conducting liquid gap (32) to the

second electrode (24) and at its phase boundary (24.1) (gas/liquid/solid) increases the concentration of the solution flowing in the liquid channel (26) as a result of anodic oxidation, with the recovery of an equivalent stoichiometric quantity of oxygen in the solution. Here, the electrons flow from second electrode (24) via the current conduction system (27,28) and the external load resistor (29) to the first electrode (23).

The same state points (ZP1 to ZP4) as in Fig. 1 are assigned to the fluid flows fed to and carried off from the reaction cell. The substance potential difference of the reaction process inside the liquid gap cell arises with their assignment and hence the inherent voltages of the reaction cell. For this, the vapor-saturated gas flow is also conveyed, with transverse removal by suction of a partial quantity, preferably in the opposite direction to the solution flow and parallel to the electrode faces through the cell.

The state points (ZP1 to ZP4) of the fluid flows are set in the external part of the substance circuit. Fig. 3 shows for example in two schematic state diagrams corresponding to one another the cyclic process carried out isobarically with an aqueous ammonia solution. The carrier gas, as the third component, only makes itself felt here via the overall system pressure (P$_T$), and is constant in the cyclic process. The saturation temperatures and

saturation pressures of the vapor component and the solution are plotted in each case over the solution concentration ξs. Similar cyclic processes can also be carried out and presented with aqueous solutions, which form water vapor as the vapor component, whereby the solutions are diluted in the galvanosorptive reaction process.

The cyclic process according to Fig. 3 contains the following changes of state: an isothermal decomposition of the solution (input ZP4s,ZP--v → output ZP1s,ZP4v), with the addition of heat, a substance-constant, internal, recuperative heat recirculation (input ZP1s → output ZP2's)/(input ZP3s → output ZP4s), a substance-constant temperature drop (input ZP2's → output ZP2s)$_p$ with heat emission and an approximately isothermal, galvanosorptive reformation of the initial solution (input ZP4v, ZP2s → output ZP3s, ZP1v) with work being released to the exterior. The vapor component enriching of the solution inside the reaction cell ($\xi_2 \rightarrow \xi_3$) is equal to the vapor component depleting of the solution outside of the cell ($\xi_4 \rightarrow \xi_1$). Normally depleting/enriching rates ($\Delta\xi$s) of the solution vary from 5% to 50% change of the vapor content. The cyclic process according to Fig.3 forms the basis for the process engineering development of the external substance circuit part, as it is represented in Fig. 4 and described below. This development of the external

substance circuit part can be applied to any thermally separable solutions in combination with a carrier gas.

The heated gas vapor enricher (42) that is combined with a first phase separator, the solution recuperator (43), the solution cooler (44), the second phase separator (45), the solution pump (46) and the gas compressor (47) are assigned to the reaction cell (40) with external load resistor (41). The routing of the substance in the circuit is as follows:

The vapor enriched two-phase mixture $[S,G,V]_3$, (ZP3) carried off from the liquid channel of the reaction cell (40) is fed to the second phase separator (45) above its bottom and is separated into the phases $[S]_3$ and $[G,V]_3$. The moderately vapor-enriched gas $[G,V]_3$ carried off at the head of the second phase separator (45) is united with the vapor-depleted gas $[G,V]_1$, (ZP1) carried off from the gas channel of the reaction cell (40), the mixture $[G,V]x$, (ZP--) is fed by the gas compressor (47) to the gas vapor enricher (42) combined with the first phase separator above the bottom and is conveyed while taking up vapor towards the heated vapor-depleting solution $[S]$. The vapor-enriched gas $[G,V]_4$, (ZP4) carried off at the head of the gas vapor enricher (42) combined with the first phase separator is fed again to the gas channel of the reaction cell (40).

The vapor-enriched solution $[S]_3$, (ZP3) carried off at the bottom from the second phase separator (45) is conveyed by the solution pump (46) through the secondary side of the solution recuperator (43), heating up to (ZP4) and introduced at the head into the gas vapor enricher (42), (ZP4) combined with the first phase separator. The vapor-depleted solution $[S]_1$, (ZP1) is carried off at the bottom of the gas vapor enricher (42), passing through the primary side of the solution recuperator (43), (ZP2') and through the solution cooler (44), (ZP2) and likewise fed to the liquid channel of the reaction cell (40). The substance supply and extraction of the galvanosorptive reaction cell is thus secured via the external part of the substance circuit with the retention of the substance potential difference.

On the process engineering components (40 to 47) of the external substance circuit part, the circled state points (ZP1) through (ZP4) are specified in Fig. 3. for each case at the substance entry and at the substance exit of the components for each individual substance flow marked with its composition [-]. They denote the changes of state of the respective substance flow inside the components (40 to 47). Intermediate states in the substance circuit on the primary-side solution exit (ZP2') of the solution recuperator (43) and of the mixed flow in the gas circuit (ZP--) have also been marked. They hardly have any

influence on the operational properties of the galvanosorptive reaction cell.

Heat is fed from the exterior to the gas vapor enricher (42) in order to deplete the enriched solution [S]r from ξ_{s4} to ξ_{s1} by vaporising. In the solution cooler (44) only so much heat is extracted from the depleted solution [S]p from $T_{2'}$ to T_2 by cooling at the lower temperature level, that the reaction process inside the galvanosorptive reaction cell (40) takes place adiabatically. The useful electrical work is extracted from the reaction cell (40) via the external load resistor (41). The drive powers of the solution pump (46) and the gas compressor (47) are small, since both conveying devices only have to replace the flow pressure losses of the complete substance circulation and are conveying with almost no differential pressure. In the process engineering structure, the external substance circuit is independent of the design of the galvanosorptive reaction cell (Fig.1 and Fig. 2).

A vapor purification by means of partial backflow condensation to be connected downstream of the gas vapor enricher (42) can be added for the case where, with the thermal separation of solutions with inherent vapor pressure of the solvent, too high a solvent vapor portion is contained in the vapor-saturated carrier gas and the latter, despite its continuous removal from the reaction cell, would hinder the galvanosorptive reaction

process inside the reaction cell. The partial backflow condensation can also be carried out recuperatively by using the surplus cooling potential of the vapor-enriched solution [S]r.

A cyclic process for thermo-galvanic energy conversion of a special kind is represented in Fig. 5. It becomes possible with external, electrostatic support of the galvanosorptive reaction process. In the two corresponding state diagrams (Fig. 5), in which the saturation temperatures (Tv, Ts) and the saturation pressures (Pv, Ps) of the solution and the vapor component are plotted over the solution concentration (ξs), a triangular process for each case is presented. The carrier gas again makes itself felt only via the constant overall system pressure (PT) of the substance circulation, whereby PTOTAL = PVAPOUR + PGAS.

The cyclic process contains changes of state: an isothermal, thermal decomposition of the solution (input ZP3s, ZP1v → output ZP3v, ZP1s), a substance-constant heating of the solution (input ZP2s → output ZP3s) with the addition of heat from the outside, and a (polytropic) galvanosorptive solution reformation (input ZP1s, ZP3v → output ZP2s, ZP1v) resulting from a superimposition of isothermal substance change and isentropic, substance-constant temperature drop with work being released to the outside.

The state points are again equilibrium states for the concerning fluid flows and are defined by their state magnitudes (P, T, ξ_s, ξ_v). The substance potential difference of the polytropic, galvanosorptive reaction process is achieved with the local assignment of the fluid flows on the reaction cell. With the additional, electrostatic support of the electrode potential, the cooling of the vapor-absorbing solution is forced with an increase of the cell working voltage. The polytropic sorption process inside the reaction cell can be guided in this case adiabatically or non-adiabatically and influenced from outside by the voltage difference conferred electro-statically on the electrodes.

The inherent cell voltage resulting from the substance potential difference of the galvanosorptive reaction cell induces the ion flow and hence the electron flow in the external electrical circuit, whilst the electrostatic voltage superimposed on the inherent voltage gives rise to the temperature drop of the vapor component-enriching solution. The additional voltage conferred electro-statically from outside is in the polytropic sorption process proportional to the temperature drop of the solution and inversely proportional to the increase in concentration of the solution. It can amount to several times the inherent voltage value of the cell. Via the working voltage of the reaction cell, its useful electrical work yield increases in proportional to

the electrostatic additional voltage. The starting and operating condition for the performance of the polytropic galvanosorptive reaction process is the presence of the inherent voltage of the reaction cell resulting from the substance potential difference.

The cyclic process according to Fig. 5 forms the basis for the process engineering development of the external substance circuit for making available the substance supply and substance extraction of the reaction cell not in equilibrium. The closed substance circuit is represented in Fig. 6 and is described below. The heated solution heater (51), the gas vapor enricher (52) combined with a first phase separator, the second phase separator (53), the solution pump (54) and the gas compressor (55) are assigned to the reaction cell (50) with external load resistor (56) and are connected with the electrostatic activation source (57). The general routing of the substance in the external circuit part applying to such ternary substance systems is as follows:

The two-phase mixture $[S,G,V]_2$, (ZP2) carried off from the liquid channel of the reaction cell (50) is fed to the second phase separator (53) above the bottom and is separated into the phases $[S]_2$, and $[G,V]_2$. The vapor-depleted gas $[G,V]_2$ carried off at the head of the second phase separator (53) is united with the moderately vapor-depleted gas $[G,V]_1$, (ZP1) carried off from the gas channel of the reaction cell (50) and the mixture

[G,V]x, (ZP--) is fed by the gas compressor (55) to the gas vapor enricher combined with the first phase separator (52) at the bottom and is conveyed with taking up vapor towards the heated vapor-depleting solution [S]₃, (ZP3). The vapor-enriched gas [G,V]₃, (ZP3) carried off at the head of the gas vapor enricher combined with the first phase separator (52) is fed again to the gas channel of the reaction cell (50).

The vapor-enriched solution [S]₂, (ZP2) carried off at the bottom of the second phase separator (53) is conveyed by the solution pump (54) through the solution heater (51), heated up to (ZP3), introduced at the head into the gas vapour enricher combined with the first phase separator (52), and the vapor-depleted solution [S]₁, (ZP1) carried off at the bottom of the gas vapor enricher combined with the first phase separator (52) is also fed again to the liquid channel of the reaction cell (50). The substance supply and extraction of the galvanosorptive reaction cell is secured via the external part of the substance circuit. The individual fluid flows of the substance circuit of Fig. 6 are given as an example for the ternary substance system hydrogen as carrier gas in combination with an aqueous ammonia solution.

With extremely small vapor component-enriching and vapor component-depleting in the solution circulation ($\Delta\xi$s < 10%) it needs to be taken into account that the inherent voltage of the

cell resulting from the substance potential difference and required for the induction of the ion flow will also be very small. In this case, the vapor-depleted solution $[S]_1$ to be fed to the reaction cell can be partially pre-cooled in a recuperator, to be provided, in the counter flow to the cooled, vapour-enriched solution $[S]_r$ and in this way the substance potential difference and thus the inherent voltage of the reaction cell can be raised.

An additional cleaning of the vapor component by means of partial backflow condensation can be added. The process engineering development of the substance circuit according to Fig. 6 is also applicable to any substance systems.

The assignment of the electrostatic activation source (62) to the electrical circuit of the galvanosorptive reaction cell (60) with polytropic reaction process is shown in Fig. 7 in an electrical equivalent circuit diagram. The activation source (62) is connected electrically parallel to the reaction cell (60) and to the consumer resistor (61). The activation source (62) consists of a variably adjustable direct current voltage source (63) and two blocking diodes (64,65) limiting the current flow to a few mA. The directions of the potentials of the reaction cell (60) and the activation source (62) are the same, just as the internal resistor (66) of the reaction cell (60) and the consumer resistor (61) are of the same resistance, whereby

the consumer resistor (61) can be adapted to the internal resistor (66) of the reaction cell (60).

If the activation source (62) is switched off, the reaction cell (60) generates its low inherent voltage $\Delta U_{st.}$ on the basis of its substance potential difference and the working current Iz flows via the consumer resistor (61) back to the reaction cell (60). The working voltage amounts here to $\Delta U_{eff.} = \Delta U_{st.} - I_{eff.} \times R_z$. When the activation source (62) is switched on, the voltage ΔU_o increases to the electrostatic voltage $\Delta U_{est.}$, while the working current portion $I_{eff.} = I_z + \tfrac{1}{2}I_D$ is flowing via the consumer resistor (61), the working current portion $(I_z - \tfrac{1}{2}I_D)$ is flowing back to the reaction cell (60) and the conducting-state current portion I_D coming from the activation source (62) is flowing back to it again. The working voltage of the reaction cell (60) amounts here to $\Delta U_{eff.} = \Delta U_{est} - (I_z - \tfrac{1}{2}I_D) \times R_z$, whereby the conducting-state current I_D ($\leq$ 10 mA) is very much smaller than the inherent cell current I_z ($\geq$ 500 mA) and thus insignificant in comparison to the inherent reaction cell current. The electrostatic voltage $\Delta U_{est.}$, resulting of the solution cooling of the polytropic reaction process, increases the electrical power of the reaction cell (60).